

Vibrational detection and control of spin in mixed-valence molecular transistors

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We investigate electron transport through a mixed-valence molecular complex in which an excess electron can tunnel between hetero-valent transition-metal ions, each having a fixed localized spin. We show that in this class of molecules the interplay of the spins and the vibrational breathing modes of the ionic ligand-shells allows the total molecular spin to be detected as well as controlled by non-equilibrium transport. Due to a *spin-dependent pseudo Jahn-Teller effect* electronic transitions with different spin values can be distinguished by their vibronic conductance side-peaks, without using an external magnetic field. Conversely, we show that the spin state of the entire molecule can also be controlled via the non-equilibrium quantized molecular vibrations due to a novel *vibration-induced spin-blockade*.

PACS numbers: 73.63.-b, 85.65.+h, 71.70.Ej, 85.75.-d

I. INTRODUCTION.

In recent years, major experimental advances have been made in contacting and measuring single molecules in three-terminal transport junctions [1], detecting the vibration [2, 3, 4], spin [4] and magnetic properties [5, 6]. Using the electrical gate to control the transport one can perform a substantial analysis of the transport processes, even when detailed microscopic information about the junction is lacking. Single-electron and coherent multi-electron tunneling processes (cotunneling, Kondo effect) governed by strong Coulomb and electron-vibration interactions allow detailed information to be extracted, as demonstrated recently for a single oligo-phenylene molecule [4, 7]. More detailed information can be accessed when mechanical control of a gateable junction [8] is possible. In the light of this progress of experimental possibilities the interesting question arises how quantum mechanical states involving both electronic and mechanical degrees of freedom may be detected and, perhaps, controlled in transport measurements. A particularly interesting aspect of single-molecule devices is the strong coupling of the electron current to the mechanical motion and the fully quantum mechanical character of this motion, resulting in Franck-Condon (FC) resonances [9, 10]. In addition, in molecular systems with magnetic ions, the spin degree of freedom becomes important [5, 6, 11, 12, 13, 14]. Thus interesting magnetic electro-mechanical effects are to be expected [15, 16].

Mixed-valence molecules exhibit this interplay of quantum nanomechanics and spin-tronics. They are crucial also as a building block for supra-molecular devices and serve as benchmark for such systems. In a mixed-valence dimer, sketched in Fig. 1, an excess electron can be localized on either of two equivalent metal ions with a local spin, thereby locally distorting the positions of the ligand atoms coordinating the ion. As the electron becomes delocalized over the molecule the distortion is “dragged” along coherently. As discussed in detail by Bersuker and Borshch this results in vibronic mixing i.e. the molecular eigenstates do not allow an adiabatic Born-

Oppenheimer (BO) separation of the nuclear and electronic motions [17]. The electronic and vibrational degrees of freedom become entangled into *vibronic states* due to a *spin-dependent pseudo Jahn-Teller* (pJT) effect. In general, pJT mixing of electronic and vibrational degrees of freedom cannot be neglected whenever electronic energy surfaces come close in energy (not necessarily degenerate as in the Jahn-Teller effect). The pronounced dependence of the delocalization, and hence of the pJT mixing, on the total spin of the molecule arises due to local direct exchange interaction on the ions (Hund’s rule), which favors the excess electron spin to be aligned with the ionic spin. Simultaneously, in such molecules this spin-dependent kinetic energy gain is responsible for the ferromagnetic double-exchange interaction [18] which competes with other types of exchange interaction.

In this paper, we present transport calculations for a model representative of a class of mixed-valence molecules. We demonstrate that a single-electron transport current can both detect and control the molecular spin due to the non-equilibrium nature of the vibrational motion. As indicated above, this does not rely on weak spin-orbit effects, but rather on strong direct, kinetic and double-exchange mechanisms. The pseudo Jahn-Teller dynamics shows up in pronounced sets of vibronic conductance peaks which depend on the spin-values of the molecular excitations. This provides a way to detect the spin without a magnetic field and probe the *in-situ* properties of a mixed-valence molecular transistor. Conversely, we show that the electronic transport current induces non-equilibrium quantized molecular vibrations which drive a pronounced population inversion among the spin-states. Such a molecule can thereby be switched to a state with a well-defined charge and spin by adjusting the applied voltages. This vibration-induced spin control arises from the interplay of spin and vibrations intrinsic to mixed-valence molecules, which may open up new possibilities for detection of mechanical motion and dissipation, magnetic switching and bistability.

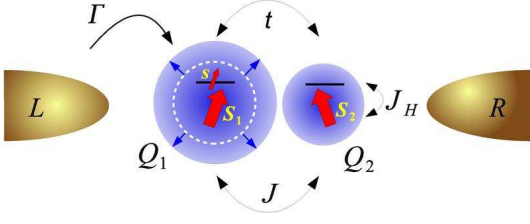


FIG. 1: Sketch: Mixed-valence dimer trapped between two electrodes, L, R . By applying a bias voltage, $V_b = \mu_L - \mu_R$, electrons can tunnel from one electrode to the other via the molecule. A third gate terminal (not shown), coupled capacitively to the molecule, effectively shifts the molecular energy levels.

II. MODEL.

We study the non-equilibrium transport properties of a well-established model for mixed-valence dimers from chemical physics, see [17, 19] and the references therein for detailed discussions. The model describes the simplest type of molecule exhibiting the spin-vibration interplay, consisting of two identical transition-metal ions, labeled by $i = 1, 2$. We account for orbital-degenerate electronic states, $|i\sigma\rangle$, where an excess electron with spin projection σ is localized on ion i . Within the molecule, the electron can tunnel with amplitude t between the ions via a mechanically stiff bridging ligand. In addition, the atomic groups that form a ligand-shell around each ion can vibrate along the local totally symmetric nuclear coordinate Q_i (breathing mode). In the absence of an excess electron, this vibration around $Q_i = 0$ is assumed to be harmonic with frequency ω . The excess electron, however, distorts the ligand-shell of the ion on which it resides, leading to a significant shift of the potential minimum of this mode (change in bond-lengths). In units of the zero-point motion energy of the vibration, this shift is equal to $\sqrt{2}\lambda$, where λ denotes the dimensionless electron-vibration coupling. In line with many experimental findings, we assume charging effects (Coulomb blockade) to be strong enough that only two molecular charge states need to be accounted for. The vibrational parts of the Hamiltonians H_{vib}^N for $N = 0, 1$ excess electrons on the molecule, written in the molecular vibrational coordinates $Q_{\pm} = (Q_2 \pm Q_1)/\sqrt{2}$, read

$$H_{\text{vib}}^0 = \sum_{i=\pm} \frac{1}{2}\omega (P_i^2 + Q_i^2), \quad (1)$$

$$H_{\text{vib}}^1 = H_{\text{vib}}^0 - \lambda\omega Q_+ + \lambda\omega Q_- (\hat{n}_1 - \hat{n}_2) + t \sum_{\sigma} (d_{1\sigma}^\dagger d_{2\sigma} + h.c.), \quad (2)$$

where $\hat{n}_i = \sum_{\sigma} d_{i\sigma}^\dagger d_{i\sigma}$ is the occupation operator of ion i and $d_{i\sigma}^\dagger$ creates an electron in state $|i\sigma\rangle$. The symmetric coordinate, Q_+ , is the *molecular* breathing mode, which couples to the total excess charge, N , of the molecule, resulting in a shift by λ of its potential surface along Q_+ .

The resulting FC transport effects have been investigated theoretically [10, 20, 21, 22] and found experimentally [2, 3, 7]. In contrast, the anti-symmetric mode, Q_- , couples to the internal charge imbalance $\hat{n}_1 - \hat{n}_2$. Together with the intra-molecular tunneling, t , this results in the pseudo Jahn-Teller (pJT) effect [17], i.e. the Hamiltonian (2) mixes electronic and vibrational states of the mode Q_- .

One of the crucial aspects in a mixed-valence molecular transistor is that the non-trivial dynamics of the Q_- mode depends on the relative orientation of the local transition-metal ion spins. The molecular Hamiltonian for $N = 0, 1$ excess electrons reads

$$H^N = H_{\text{vib}}^N - J\mathbf{S}_1 \cdot \mathbf{S}_2 - J(\mathbf{s}_1 \cdot \mathbf{S}_2 + \mathbf{S}_1 \cdot \mathbf{s}_2) - \sum_{i=1,2} J_H \mathbf{S}_i \cdot \mathbf{s}_i. \quad (3)$$

The intra-ionic Hund interaction, J_H , couples the spin of the excess electron, $\mathbf{s}_i = \frac{1}{2} \sum_{\sigma, \sigma'} d_{i\sigma}^\dagger \boldsymbol{\sigma}_{\sigma\sigma'} d_{i\sigma'}$, to the spin of the transition-metal ions, \mathbf{S}_i , where $\boldsymbol{\sigma}$ denotes the vector of Pauli-matrices and $\mathbf{s}_i = 0$ if no electron is present on ion i . Together with the intra-molecular tunneling, t , incorporated in Eq. (2), the intra-ionic Hund interaction results in a double-exchange splitting $2t_S$ of eigenstates with total molecular spin S [18]:

$$\frac{t_S}{t} = \frac{S + \frac{1}{2}}{2S_1 + 1} \leq 1, \quad (4)$$

where $S_1 = S_2$ denotes the spin-length of the equivalent ions ($\mathbf{S}_1, \mathbf{S}_2$). Result (4) for the effective tunneling strength t_S is obtained by expressing H^1 in the electronic basis of total spin eigenstates using vector coupling coefficients. In the semi-classical limit of large ionic spins [18], $S_1 \gg 1$ (not considered further below), this reduces to $t_S/t = S/2S_1 = \cos(\theta/2)$, where θ is the angle between the two classical ionic spins. This makes clear that the kinetic energy which can be gained by the excess electron is maximal for parallel ionic spins due to the strong intra-ionic coupling and is suppressed by $\cos(\theta/2)$, i.e. by the electron spin-eigenfunction component quantized in the direction of the ionic spin. Importantly, in mixed-valence molecules J_H is much larger than the other energy scales, $J_H \gg |J|, \omega, t$ (typical values: $J_H \sim 1$ eV, $J, t \sim 1$ -100 meV, $\omega \sim$ tens of meV) [17, 23, 24]. This scale separation derives from the intra-ionic origin of J_H (direct Hund exchange), in contrast to the intra-molecular processes involved in the exchange J and hopping t . We assume a ferromagnetic coupling, $J_H > 0$, i.e. a less than half filled ionic shell. The excitations where \mathbf{S}_i and \mathbf{s}_i are aligned anti-parallel can therefore be neglected. Eq. (3) also incorporates the intra-molecular coupling J of the spins of different ions. From hereon we take the length of the ionic spins to be $S_1 = S_2 = 1/2$. The Hamiltonian for the charged molecule consists of an $S = 3/2$ and an $S = 1/2$ diagonal block, with $2S + 1$ sub-blocks on the diagonal, given by

$$H_S^1 = H_{\text{vib}}^1|_{t=t_S} - \frac{1}{2}JS(S+1) + \text{const.} \quad (5)$$

This makes explicit the interesting property of mixed-valence molecules, that the strength of the pJT effect depends on the total molecular spin S [17] due to the competition between the local distortion (coupling $\lambda\omega$) and the effective delocalization of the electron (energy t_S). For $N = 1$ we numerically diagonalize the blocks separately for each spin state S to obtain the molecular eigenstates, which are not of the adiabatic BO form. For $N = 0$ the states trivially factorize in BO form.

III. TRANSPORT.

The interplay of vibrational and spin degrees of freedom can be demonstrated for the basic transistor setup, sketched in Fig. 1, described by the transport Hamiltonian $H = H_{MV} + H_T + H_{res}$. Here $H_{MV} = \sum_{N=0,1} X^N H^N X^N - \alpha V_g N$, where X^N projects onto states with charge N and α is the gate coupling. The electrodes $r = L, R$ at electrochemical potential $\mu_r = \mu \pm V_b/2$ and temperature T are described by

$$H_{res} = \sum_{r=L,R} \sum_{k,\sigma} (\epsilon_k - \mu_r) c_{rk\sigma}^\dagger c_{rk\sigma}, \quad (6)$$

i.e. V_b is the bias voltage, and couple to the molecule by

$$H_T = \sum_{r=L,R} \sum_{i=1,2} \sum_{k,\sigma} T_r^i d_{i\sigma}^\dagger c_{rk\sigma} + h.c.. \quad (7)$$

Here $c_{rk\sigma}^\dagger$ creates an electron with spin σ in state k of electrode r and T_r^i is the amplitude for tunneling to ion i of the dimer. We assume a sequential arrangement i.e. $T_L^1 = T_R^2 = \sqrt{\Gamma/(2\pi\rho)}$ and $T_L^2 = T_R^1 = 0$, which may experimentally be favored by appropriate design of “clipping” ligands. Here Γ denotes the tunneling rate.

In three-terminal molecular junctions, the tunneling rate can be as small as $\Gamma \approx 0.1$ meV and is often the smallest energy scale in the problem, enabling accurate spectroscopy of e.g. molecular vibrations [7]. We focus on the regime of voltages and temperatures ($T \approx 10\Gamma$) where single-electron tunneling dominates the transport as is the case in many experiments [2, 3, 4, 5, 6, 7]. Using a kinetic (master) equation we calculate the non-equilibrium stationary state occupations of the molecule for each charge (N) and spin multiplet (S), keeping track of the symmetric vibrational (Q_+) quantum number as well as the quantum number for the entangled state of the electrons and the anti-symmetric vibrations (Q_-). For weak tunnel coupling the transport rates can be evaluated in lowest non-vanishing order in H_T (i.e. Fermi’s Golden Rule). Additionally, we account phenomenologically for relaxation due to coupling to a dissipative environment (e.g. substrate phonons). We assume an energy-dependent density of states (rate $\gamma^{s(v)}(E) = \gamma_0^{s(v)} \cdot (E^2/\omega^2)$) for transitions between states with equal spin (γ_0^s) and different spin (γ_0^s). The latter relate to spin-orbit coupling effects and are therefore

assumed to be much smaller than the former, $\gamma_0^s \ll \gamma_0^v$. The strength of the spin-allowed relaxation of course depends on the type of the molecular vibration mode and the junction substrate. For examples and discussion of very slow relaxation in the context of photon-tunneling in single-molecule junctions, see [25] and the references therein.

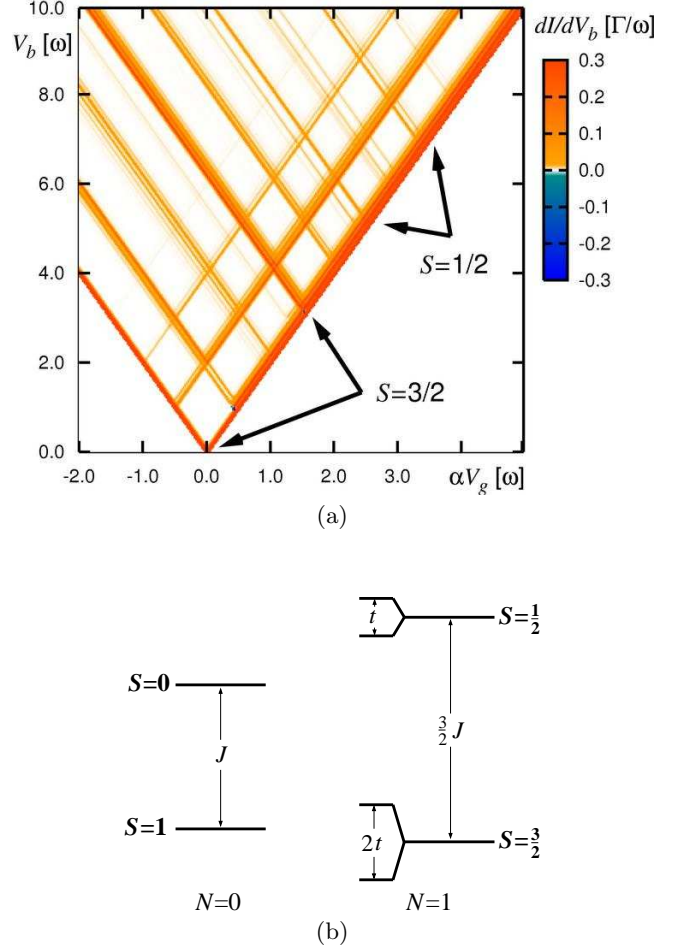


FIG. 2: (color online) (a) Differential conductance (dI/dV_b) for V_g vs. V_b ($J = 2.9\omega$, $t = 1.5\omega$, $\lambda = 0.5$, $\Gamma = 9 \cdot 10^{-4}\omega$, $\gamma_0^v = 3.2 \cdot 10^{-3}\Gamma$, $\gamma_0^s = 10^{-4}\Gamma$, $T = 10^{-2}\omega$) (red: $dI/dV_b > 0$, blue: $dI/dV_b < 0$). The double-exchange coupling leads to a spin-dependent gap size of the vibronic spectrum (see arrows). The spectrum of $S = 3/2$ is harmonic (signalled by equidistant resonance lines of small energy separation), while the one of $S = 1/2$ is anharmonic (non-equidistant lines). (b) Sketch of energy spectrum: The spin-multiplets are split due to the intra-molecular coupling J . For $N = 1$, each spin-multiplet is split again by approximately twice the spin-dependent intra-molecular tunneling, t_S , due to the pJT effect. Vibrational / vibronic excitations are omitted for clarity.

IV. RESULTS.

A. Spin-dependent pseudo Jahn-Teller effect: Identifying spin values.

The differential conductance as function of the applied voltages is shown in Fig. 2(a), using a set of parameters representative for mixed-valence dimers with weak electron-vibration coupling and ferromagnetic intra-molecular coupling: $J = 2.9\omega$, $t = 1.5\omega$, $\lambda = 0.5$. The transport spectrum displays a number of sharp, well-separated resonance lines, which are “dressed” by many more lines with small separations. Two pronounced pairs of excitations appear, corresponding to the $S = 1/2$ and $S = 3/2$ spin-multiplets which are split due to the intra-molecular coupling J (c.f. Eq. (5)). Each multiplet is split approximately by twice the spin-dependent intra-molecular tunneling t_S , leading to a double-exchange gap which is reduced by a factor 2 for the $S = 1/2$ state ($t_{1/2} = t_{3/2}/2$, see also Fig. 2(b)). More generally, the spin parameters can be determined from the ratios of the intra-molecular splittings giving $t_S/t_{S-1} = (S + 1/2)/(S - 1/2)$. A central result of this work is that an independent check of this assignment of the spin is provided by the vibronic lines “dressing” the above excitations. This type of excitations arises when the *shape* of the vibrational potentials has a significant charge dependence [22]. Here their occurrence indicates a significant pJT mixing in the $N = 1$ charge state which changes the frequency and additionally induces anharmonicity in the effective adiabatic potentials. If the pJT effect is weak (as for $S = 3/2$), these potentials are approximately harmonic in both charge states, and the spacing between these lines (that are due to transitions between excited vibrational and vibronic states) is even and equals the small frequency *difference*. For a stronger pJT effect ($S = 1/2$) the potential in the $N = 1$ charge state becomes anharmonic and the lines are unevenly spaced. Clearly, in Fig. 2(a) the “dressing” of the lower pair of lines is more evenly spaced than the upper set of lines, confirming the assignment of high spin state at low energy. Here we merely note that a detailed analysis of the pJT transport resonances allows the electro-mechanical parameters t_S, λ, ω to be determined quantitatively, by reading off the voltage positions of the resonances. Also, we have invoked an adiabatic picture for the interpretation, which has only an approximate validity, and some qualitative transport effects violate it. This is, however, not essential here, see [26] for details. The spin identification works very well for $t \gtrsim \lambda^2\omega$, i.e. when the pJT effect is weak to moderate (for $|J| \gtrsim t$ the resonances of the two spin-multiplets can be considered as separate). Thus the intra-molecular ferromagnetic coupling is revealed by the transport spectrum at zero magnetic field, by double-exchange and vibronic effects. Finally, we note that the energy average of the total S multiplets split by double-exchange follows JS , providing a third, independent check of the spin value assignment.

B. Current blockade and spin switching.

For a wide range of parameters, the model exhibits a second, even more striking effect, exemplified for $J = 0.5\omega$, $t = 5.0\omega$, $\lambda = 1.5$ in Fig. 3(a). At low energies, the current is stepwise *reduced* when going deeper into the sequential tunneling region leading to negative differential conductance (blue lines in Fig. 3(a)). Simultaneously, the occupation of the molecular state with zero-spin and no vibrational excitations grows, reaching over 90% (see Fig. 3(b)). Within this region the current is strongly suppressed due to the pronounced population inversion that stabilizes the charge to $N = 0$ and the spin to $S = 0$. This *vibration-induced spin-blockade* provides another indication for the spin properties of the mixed-valence molecule and additionally allows the spin to be controlled electrically. The effect is readily understood by considering the non-equilibrium vibrations induced by the electric current. First we note that in the low-bias region where the spin-blockade occurs, the direct transition by electron tunneling from $S = 1 \rightarrow S = 1/2$ is energetically not yet possible and the transition $S = 0 \leftrightarrow S = 3/2$ is generally forbidden by spin selection rule ($\Delta S = \pm 1/2$). Now consider an electron which has just enough energy to excite a vibrational, Q_+ , (or vibronic, Q_-) quantum, when entering / leaving the molecule ($N = 0 \leftrightarrow 1$). If the molecule does not immediately relax it can accumulate more quanta in subsequent tunneling processes as sketched in Fig. 3(c). Eventually, when a sufficient amount of vibrational energy has been accumulated a low energy electron can be assisted to excite the molecular spin-system. This tunneling process brings the molecule to a lower spin state with $S = 1/2$. Finally, the molecule can relax to the $S = 0$ state by a single tunneling process in which the excess energy is dissipated into the electrodes. Now the molecule is trapped in a state with fixed charge $N = 0$ and spin $S = 0$ and the current is suppressed: neither the $S = 3/2$ states (due to the spin selection rule) nor the $S = 1/2$ state (due to the low bias voltage $V_b \lesssim (J+t) - 2V_g$ and a strong Coulomb interaction on the molecule) are accessible. Fig. 3(b) shows that the spin-blockade is lifted at higher bias $V_b \approx (J+t) - 2V_g$ where the direct process back to $S = 1/2$ becomes possible, thereby confirming the above mechanism.

Clearly, the vibration induced spin-blockade is expected to break down when the excited spin state is too high in energy to be reached or when escape processes from $S = 0$ become dominant already at low bias voltages. The escape processes, however, have to change the spin by *at least* 1 quantum and are therefore parametrically weak, since they relate to spin-orbit coupling ($\gamma_0^s \ll \gamma_0^v$) or higher order tunneling processes. For instance, the phenomenological spin-flip relaxation which we included is responsible for the small remnant current in the spin-blockade region. Secondly, the blocking state has to be reached: the single-electron transport current “pumps” the vibrational system (rate $\propto \Gamma$) when the temperature is lowered below the vibrational

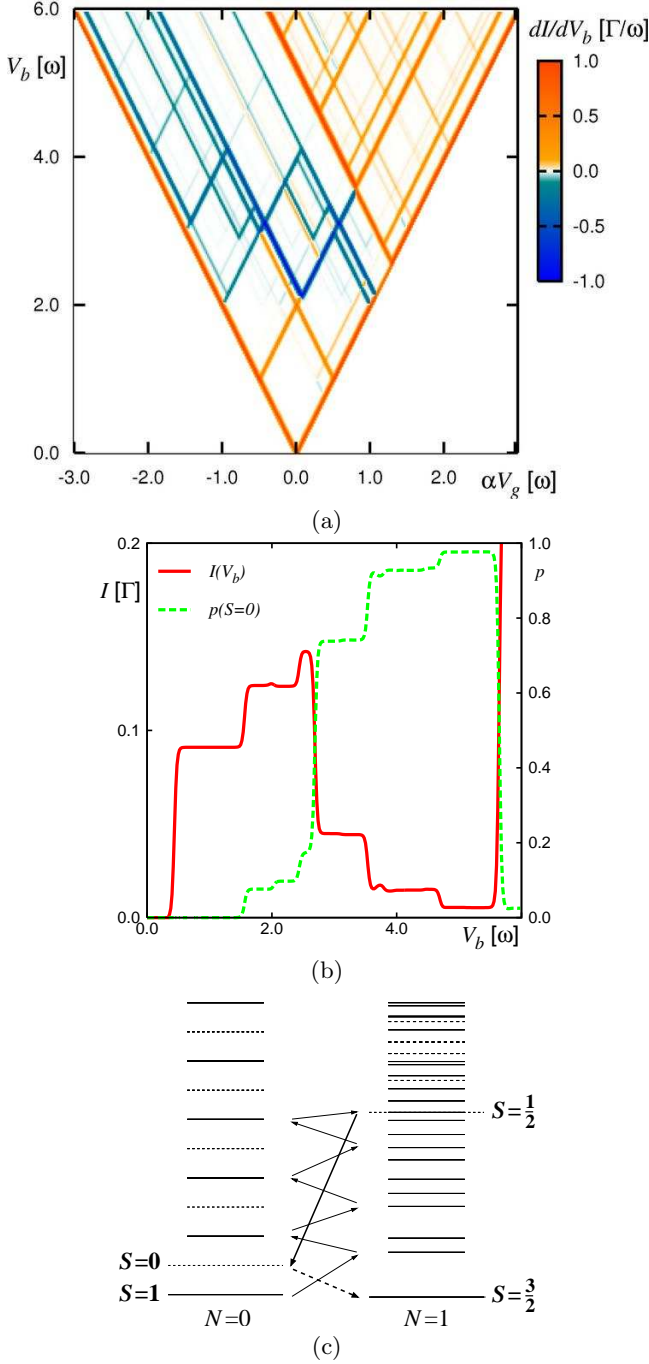


FIG. 3: (color online) (a) Differential conductance (dI/dV_b) for V_g vs. V_b ($J = 0.5\omega$, $t = 5.0\omega$, $\lambda = 1.5$, $\Gamma = 9 \cdot 10^{-4}\omega$, $\gamma_0^v = 1.8 \cdot 10^{-2}\Gamma$, $\gamma_0^s = 10^{-4}\Gamma$, $T = 10^{-2}\omega$). (b) Current vs. V_b (red solid) at $V_g = -0.2\omega$ and probability of $S = 0$ multiplet with no vibrational/vibronic quanta excited (green dashed). (c) The energy spectrum of the $N = 0, 1$ charge states and the spin-blockade mechanism. The line-style distinguishes the total spin values S of the states. The longer lines denote a vibrational/vibronic groundstate whereas the shorter ones are excited by at least one such quanta. The molecule is “pumped” by a sequence of tunneling events, each time changing the charge and exciting vibrational and / or vibronic quanta until the $S = 1/2$ spin state is reached. From there, the molecule falls into the blocking state ($S = 0$ vibrational groundstate) via another tunnel process. Since the transition to $S = 3/2$ is forbidden by spin-selection rules, $S = 0$ cannot relax and the current strongly suppressed.

frequency ω (preventing thermal relaxation) and when the tunnel coupling is sufficiently weak. It is thus crucial that the intra-molecular vibrations are not strongly damped. However, relaxation rates can compete with the transport rates without destroying the vibration-induced spin-blockade as long as the $S = 1/2$ state can still be efficiently reached using the vibrations. For the results we present here this is indeed the case. Finally, cotunneling processes are expected to affect both the access to and the escape from the blocking state. A full calculation of this effect is possible in principle [27], but is prohibited by the large number of states required here to describe the vibration-induced spin-blockade. Inspection of the numerically calculated rates to second order in Γ for a truncated spectrum indicates that the presented results are robust against perturbations due to higher-order tunneling. Importantly, these processes can be suppressed by reducing the tunneling coupling by appropriate choice of connecting ligand groups.

We note that in this paper we have discussed the case of ferromagnetic intra-molecular coupling J . However, the vibration-induced spin-blockade is generic and also occurs for anti-ferromagnetic coupling $J < 0$ provided that $t > |J|$ and in this case leads to a stabilized *excess charge* $N = 1$ and *high spin* $S = 3/2$.

V. CONCLUSIONS.

Using a representative model we have demonstrated that transport through a mixed-valence molecular transistor entails an interplay of delocalized excess electrons, localized ionic spins, ligand-shell vibrations and Coulomb blockade. For this class of molecules transport-induced intra-molecular vibrations depend on the spin and their energy can be transferred to the spin-system at specific voltages, subsequently “locking” the spin, vibration and charge in a well-defined state. The generic model, analyzed here in a non-equilibrium situation, relates naturally to mixed-valence molecules [17] such as $\text{Ru}^{2+,3+}$ complexes with pyridine organic ligands of the Robin-Day class II or III. The effects predicted here provide several bridges between nano-electromechanical systems (NEMS) and spintronic devices and applications in this direction can be envisaged. Clearly, the predicted spin-blockade effect will be sensitive to local magnetic fields, mechanical energy dissipation and spin-orbit effects and sensing applications involving these can be considered. Also, the blockade effect indicates slow transport dynamics: this may be used in the context of switching and bistable operation of molecular transistors by sweeping voltages non-adiabatically, with the new possibility of magnetic field control due to the involvement of spin. Finally, from a chemistry perspective, transport measurements provide unique insight in the degree of electron delocalization determining the key properties of mixed-valence molecules *embedded* in an electric circuit. Thus the investigation of complex mixed-valence systems as

devices [28] proves to be an interesting avenue in single-molecule electronics.

We acknowledge H. Schoeller, P. Kögerler, and H.

Luecken for stimulating discussions and the financial support from DFG SPP-1243, the NanoSci-ERA, the Helmholtz Foundation, and the FZ-Jülich (IFMIT).

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- [1] H. Park, A. K. L. Lim, A. P. Alivisatos, J. Park, and P. L. McEuen, *Appl. Phys. Lett.* **75**, 301 (1999).
 - [2] H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alivisatos, and P. L. McEuen, *Nature* **407**, 57 (2000).
 - [3] A. N. Pasupathy, J. Park, C. Chang, A. V. Soldatov, S. Lebedkin, R. C. Bialczak, J. E. Grose, L. A. K. Donev, J. P. Sethna, D. C. Ralph, et al., *Nano Lett.* **5**, 203 (2005).
 - [4] E. A. Osorio, K. O'Neill, M. R. Wegewijs, N. Stuhr-Hansen, J. Paaske, T. Bjørnholm, and H. S. van der Zant, *Nanolett.* **7**, 3336 (2007).
 - [5] H. B. Heersche, Z. de Groot, J. A. Folk, H. S. J. van der Zant, C. Romeike, M. R. Wegewijs, L. Zobbi, D. Barreca, E. Tondello, and A. Cornia, *Phys. Rev. Lett.* **96**, 206801 (2006).
 - [6] M.-H. Jo, J. E. Grose, K. Baheti, M. M. Deshmukh, J. J. Sokol, E. M. Rumberger, D. N. Hendrickson, J. R. Long, H. Park, and D. C. Ralph, *Nano Lett.* **6**, 2014 (2006).
 - [7] E. A. Osorio, K. O'Neill, N. Stuhr-Hansen, O. F. Nielsen, T. Bjørnholm, and H. S. van der Zant, *Adv. Mater.* **19**, 281 (2007).
 - [8] A. R. Champagne, A. N. Pasupathy, and D. C. Ralph, *Nano Lett.* **5**, 305 (2005).
 - [9] K. Flensberg, *Phys. Rev. B* **68**, 205323 (2003).
 - [10] A. Mitra, I. Aleiner, and A. J. Millis, *Phys. Rev. B* **69**, 245302 (2004).
 - [11] C. Romeike, M. R. Wegewijs, W. Hofstetter, and H. Schoeller, *Phys. Rev. Lett.* **96**, 196601 (2006).
 - [12] C. Romeike, M. R. Wegewijs, and H. Schoeller, *Phys. Rev. Lett.* **96**, 196805 (2006).
 - [13] C. Romeike, M. R. Wegewijs, W. Hofstetter, and H. Schoeller, *Phys. Rev. Lett.* **97**, 206601 (2006).
 - [14] J. E. Grose, E. S. Tam, C. Timm, M. Scheloske, B. Ulgut, J. J. Parks, H. D. Abruna, W. Harneit, and D. C. Ralph, *Nature Materials* **7**, 884 (2008).
 - [15] D. Fedorets, L. Y. Gorelik, R. I. Shekhter, and M. Jonson, *Phys. Rev. Lett.* **95**, 057203 (2005).
 - [16] P. S. Cornaglia and D. R. Grempel, *Phys. Rev. B* **71**, 245326 (2005).
 - [17] I. Bersuker and S. Borshch, *Vibronic Interactions in Polynuclear Mixed-Valence Clusters* (Wiley, 1992), vol. 81 of *Advances in Chemical Physics*, chap. 6, p. 703.
 - [18] P. W. Anderson and H. Hasegawa, *Phys. Rev.* **100**, 675 (1955).
 - [19] I. B. Bersuker, *Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory* (Wiley-Interscience, 1996).
 - [20] S. Braig and K. Flensberg, *Phys. Rev. B* **68**, 205324 (2003).
 - [21] J. Koch and F. von Oppen, *Phys. Rev. Lett.* **94**, 206804 (2005).
 - [22] M. R. Wegewijs and K. C. Nowack, *New J. of Phys.* **7**, 239 (2005).
 - [23] S. B. Piepho, E. R. Krausz, and P. N. Schatz, *J. Amer. Chem. Soc.* **100**, 2996 (1978).
 - [24] S. Borshch and I. Kotov, *J. Struct. Chem.* **32**, 35 (1991).
 - [25] A. Volokitin and B. Persson, *Rev. Mod. Phys.* **79**, 1291 (2007).
 - [26] F. Reckermann, M. Leijnse, M. R. Wegewijs, and H. Schoeller, *Eur. Phys. Lett.* **83**, 58001 (2008).
 - [27] M. Leijnse and M. R. Wegewijs, *Phys. Rev. B* **78**, 235424 (2008).
 - [28] E. Bominaar, C. Achim, S. Borshch, J. Girerd, and E. Münck, *Inorganic Chemistry* **36**, 3689 (1997).